PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Recovery of Sterols, Antioxidants and other Unsaponifiable Components

We, PITTSBURGH PLATE GLASS COMPANY, a Corporation organised under the laws of the State of Pennsylvania, United States of America, of One Gateway center, Pittsburgh 22, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to methods of obtaining sterols and antioxidants suitable for various applications such as intermediates in the preparation of wetting agents, pharmaceuticals, preservatives of food products and other products subject to deterioration by reason of oxidation. The invention has particular relation to the recovery of sterols, antioxidants and other unsaponifiable components from concentrates derived from a glyceride oil such as soybean oil or related products.

The tocophenols which are anti-oxidants are also called Vitamin E. The materials are of interest for nutritional and medicinal uses and a large scale convenient method for their isolation would be of great value.

It has heretofore been recognized that some of the glyceride oils, notably soybean oil, contain, in addition to a complex mixture of fatty acid triglycerides and free fatty acids, small amounts of unsaponifiable compounds such as sterols, tocopherols and other constituents. Many of these unsaponifiable constituents were, if recoverable, recognized to be of great value in the preparation of inhibitols or antioxidants for food products or emulsifiers and in some cases, in the preparation of pharmaceuticals such as sex hormones. However, prior to the present invention no suitable process applicable on a large or commercial scale for their preparation has been available. For these reasons some of the materials, although much in demand have remained extremely expensive and the use thereof by the general public has been limited.

The present invention relates to a process whereby the sterols, antioxidants and other unsaponifiable constituents of the natural glyceride oils or related products are recoverable economically and in large quantities. According to the process a concentrate of fatty acids or glycerides and sterols produced according to various methods and containing in excess of 3% by weight of unsaponifiable matter is subjected to the steps of saponifying the fatty acids or the glycerides of fatty acids associated with the sterols and the antioxidants in soybean oil by means of a suitable alkali, making up the soaps into solution with water and a lower alcohol in such concentration that no emulsions are obtained when contacted with an extracting solvent, then extracting the unsaponifiable constituents in counter-current fashion from the soap solution by application of a solvent such as naphtha, an ether or a chlorinated hydrocarbon or any other solvent of the unsaponifiable matter, which is substantially insoluble or but slightly soluble in the mixture of water, alcohol and soap.

Furthermore according to a preferred embodiment of this invention substantial economies in the use of alcohol in the water-alcohol phase of the system and enhanced speed and smoothness of operation, can be attained in a counter-current system for extracting unsaponifiable matter from soaps in a solution of water and a water soluble alcohol, by the addition of a water soluble alcohol to the solvent of unsaponifiable matter in a zone at or near the inlet end for the solvent. This added lower alcohol can be included in the feed of solvent of unsaponifiable

matter, or it can be introduced through an inlet contiguous to, or near the solvent inlet, but below the inlet for soap solution. When so introduced, it promotes phase separation and reduces the tendency to emulsification and flooding. Systems which otherwise would be practically inoperative for countercurrent extraction are rendered operative by addition of small proportions of lower acohol at or near the bottom of the extraction zone. The concentration of the alcohol in the lower zones near the outlet for the soap solutions is thus increased.

For a better understanding of the invention reference may now be had to the accompanying drawings in which the single figure diagrammatically illustrates a convenient process of effecting the various extractions involved in or applicable in the practice of the invention.

In the practice of this invention, various products comprising soybean oil glycerides or fatty acids or soaps of fatty acids or mixtures of these, and unsaponifiable materials in sufficient concentration may be employed as starting materials. These may be derived from several sources. For example, in certain processes of extracting oils such as those disclosed in Patent No. 658,967, glyceride oils, such as soybean oil, were subject to treatment with selective polar solvents such as furfural or ethyl aceto acetate, having preferential solvent action to the more unsaturated components of the glyceride oils. The sterols and inhibitols of soybean oil are selectively dissolved by the polar solvent so that the extract fraction resulting from the application of the process is substantially enriched in these components.

It is usually practicable thus to extract 20 to 80 per cent of the original oil as a solution in a polar solvent such as anhydrous furfural. The solvent can be removed from this solution with the further concentration of the unsaponifiables and the mixture, then saponified with alkali and treated under the provisions of the present invention to recover unsaponifiables. However, in most instances, it is preferable first to selectively remove the major portion of the glyceride oil components from the solution for other uses, at the same time further concentrating the unsaponifiable matter with respect to the glyceride oil remaining in solution. Various methods of effecting such concentration are available.

One convenient method, however, involves selectively extracting the glycerides of the fatty acids from the polar solvent solution by means of a solvent immiscible with or only partially miscible with the polar solvent. Naphtha constitutes one such solvent. Preferably, naphtha of paraffinic character is employed and it may comprise hydrocarbons of various molecular weights containing, for example, 6 to 10 carbon atoms in the molecule. However, a heptane to decane fraction has been found to operate efficiently in the system. In most instances, it is advisable to strip off a portion of the polar solvent, such as furfural, from the extract solution by distillation before washing the solution with naphtha. Sufficient solvent may be distilled to form a 20 to 50% solution by weight of oil in furfural. The remaining extract solution may then be washed with naphtha within a ratio of approximately .2 to 10 parts by volume per part of original oil extracted. The operation may be conducted countercurrently in a suitable column or may be conducted batchwise. Preferably, the temperature of operation is within an approximate range of 45 to 95° F. though variations of five or ten degrees higher or lower are contemplated.

As a result of the washing of the extract solution of oil dissolved in polar solvents, nearly all of the glyceride oils are extracted out into the naphtha solution. The naphtha from this solution may be evaporated and the oil recovered for use as a drying oil or for other purposes. There remains in the polar solvent a concentration of the free fatty acids and the unsaponifiable matter and some glyceride oils. This latter portion, hereinafter called "by-product", is small with respect to the original oil extracted but is, of course, considerable with respect to the small amount of unsaponifiable matter. The free fatty acids, unsaponifiables and glyceride oils may be recovered from the polar solvent solution by evaporation of the solvent. It is also permissible to extract them out with an excess of naphtha and then to evaporate the naphtha. The composition of the recovered portion is approximately as follows:—

5 to 40 percent by weight free fatty acid

4 to 30 percent by weight unsaponifiable matter

The remainder—glyceride oils and other constituents.

If preferred, a concentrate of the unsaponifiable matter, free fatty acids and a small amount of glyceride oil may be recovered from an extract product oil by contacting this extract oil with a wet polar solvent, such as a saturated or nearly saturated solution of furfural and water. Conveniently, this extraction can be conducted at a temperature of about 60 to

90° F. Before the aqueous furfural extraction, all or much of the original polar solvent, such as furfural, employed in initially treating the original oil, may be eliminated by distillation.

As a result of the extraction of the original extract oil with wet polar solvents such as furfural, the free fatty acids, unsaponifiable matter and a small amount of glycerides are extracted in the wet solvent. The glycerides of the free fatty acids are relatively insoluble and separate out as a layer which can be recovered for other purposes. The remaining concentrate or "by-product" of unsaponifiable matter, free fatty acids and residual glyceride oils or glycerides of free fatty acids may be recovered by evaporation of the solvents and are of much the same composition as that recovered by the extraction of the polar solvent extract with naphtha.

Another appropriate source material of unsaponifiable matter suitable for use in the practice of the present invention comprises the so-called soap stocks and "foots" acids resulting from the refining of soya oil with small amounts of alkali. In this refining operation, small amounts of free fatty acids and gycerides of soya oil are converted into soaps, and when these are separated off, it has been found that a high percentage of the unsaponifiable matter and notably of the sterols, of which stigmasterol is one of the more important are retained in the soap stock fraction. Soap stocks also include considerable amounts of unsaponified glycerides as well as substantial amounts of water. A typical composition of a soya soap stock is given on page 834 in the book "Soybeans and Soybeans Products", Volume II by Klare S. Markley. When recovered, the free fatty acids liberated are of considerable value.

In accordance with this invention, these foots can be treated with alkali such as sodium hydroxide, or other sources of mixture of soybean acids or soybean glycerides rich in unsaponifiable matter such as sterols and tocopherols are available and may be used as starting materials in the practice of the present invention. Some such additional sources include:—

1. Distillation residue from distillation of soya acids.

2. Extraction of oil bearing soya meal with hot ethanol or a mixture of methanol and hexane. When the solution cools a concentrate of unsaponifiable matter exists in the alcohol layer.

3. The distillate from the molecular distillation of soybean oil.

4. In the treatment of soya oil with absorbants such as fuller's earth or activated clay, unsaponifiable matter is selectively absorbed and the resultant concentrate of unsaponifiable matter can be extracted out from the absorbant, after the latter has been filtered off, by treating the absorbant with naphtha or other solvents. When the naphtha is evaporated, the concentrate is recovered.

5. A concentrate of unsaponifiable matter is obtained by liquid extraction of soya oil with a lower aliphatic alcohol of one to three carbon atoms such as methanol, ethanol, propanol or isopropanol.

6. Concentrates of unsaponifiable matter distill off when the soya oil is vacuum deodorized by blowing with steam.

7. Fatty acids from saponification and subsequent acidification of soya oil or by hydrolysis of soya oil, or soya soap stocks may be extracted, for example, with furfural and naphtha, to provide a concentrate very rich in unsaponifiable matter.

8. A concentrate of unsaponifiable matter prepared by the extraction of soya oil with liquid propane.

All of these materials containing about 3% and upward of unsaponifiables can be employed as starting materials in the practice of this invention. The concentrates can be saponified with alkali, made up into an appropriate solution in water and a lower water soluble, monohydric alcohol and then they can be countercurrently extracted with naphtha or other solvent of unsaponifiable matter which is at least partially immiscible in the soap solution.

Likewise, it is possible to obtain even further preliminary concentration of the unsaponifiable matter and thus to reduce the volume of soap solution extracted by splitting the glycerides in a concentrate of unsaponifiable matter such as a soap stock or a by-product from solvent extraction of soya oil, and then fractionally distilling off free fatty acids. Such splitting may be effected by saponifying the concentrate with alkali and then acidifying the resultant soaps. The acids can also be liberated by hydrolization or by Twitchellization or similar methods. A large amount of the fatty acids can then be distilled. As a result of this operation, the unsaponifiable matter, and notably the sterols, are even further concentrated in the still residue. This residue may then be subjected to treatment with alkali in order to resaponify the free fatty acids and glycerides remaining, and the mixture of soaps and unsaponifiable matter may be made up into solution and extracted in the manner above described.

Summarizing, the compositions to be treated according to the invention have the following composition: (upon a water free basis):—

3—50% by weight unsaponifiable matter

5—70% by weight of free fatty acids or soaps

The remainder—glyceride oils and other constituents.

These compounds are saponified and the saponified mixture comprises in addition to water and alkali, the following:—

5 —35%	of soybean oil concentrate (in a saponified form)
10 —40%	of methanol, ethanol, isopropanol, or propanol
30 —85%	water
0.5— 7.0%	of alkali (as soaps or free)

Extraction of an alcohol solution of such a saponified mixture with naphtha or like solvent may be effected in an apparatus such as an extraction column of the type disclosed in the present drawings. It may also be effected by continuously feeding naphtha and soap solution into a centrifuge of the so-called Podbieniak type. The solution in the latter is fed in at the axis and naphtha in at the outer periphery. The denser component (soap solution) permeates outwardly along an involutely coiled perforated diaphragm in the centrifuge and the naphtha permeates inwardly in continuous counter-current flow. The naphtha phase is drawn off at the axis of the centrifuge and the soap solution is drawn off at the periphery.

A suitable embodiment of apparatus for use in the practice of the invention is illustrated in the drawings and comprises Columns I and II. A soap solution of unsaponifiable concentrate may be fed into Column I near the top thereof as indicated at 3 and a naphtha solution is fed in near the bottom as indicated at 4. Soap solution from which the extract of unsaponifiable matter has been removed is drawn off from the bottom of the column as indicated at 5 and passes to a still 6 for removal of the solvents contained therein. The soaps may then pass through a line 7 to a container 8 where the soaps are acidified in order to regenerate the free fatty acids. Such acids are drawn off as indicated at 9 and passed to a container 10 for storage or for further treatment.

The solution of unsaponifiable matter in naphtha is drawn off at the top of Column I as indicated at 11 and passes to a zone slightly above the bottom of Column II. Simultaneously, water is fed into the top of Column II as indicated at 12 in order to wash out residual soaps from the concentrate of unsaponifiable matter. The naphtha solution of concentrate is drawn off as indicated at 13 at the top of Column II. Simultaneously, the water solution of soaps and other water soluble constituents is drawn off as indicated at 14, and may be subjected to further treatment. The naphtha solution of unsaponifiable matter passing out at 13 may be subjected to further treatment, for example to evaporation in order to eliminate the naphtha contained therein.

The proportioning of the several components in the centrifuge or in the Column I will vary to some degree for different alcohols as solvents. However, the ranges are fairly nearly coextensive and overlap each other over much of their extent. With alkyl monohydric alcohols containing 1 to 3 carbon atoms, e.g. methyl, ethyl isopropyl and propyl alcohol, the proportions usually will fall apprximately within the ranges specified in the examples which are to follow. In most instances, the proportions in the solutions comprising water and an alcohol of 1 to 3 carbon atoms may vary. A good average statement of proportions in the final feed solution for any of these alcohols will be approximately as follows:—

	Parts by weight
Saponified sterol concentrate	100 (upon a water free basis)
Water	146 to 1460
Alcohol of 1 to 3 carbon atoms	61 to 610

Naphtha preferably is employed in a ratio of 1 to 10 parts by volume per part of soap solution.

The temperature of operation of the system may be almost any from approximately normal room temperature or thereabouts up to that at which one or more components of the system tend strongly to volatilize off.

The temperature should not exceed the boiling point of any component of the system. A range of about 100 to 160 or 180° F. is preferred.

The flow of solvent of unsaponifiable matter, e.g., naphtha, may be within a range of about 1 to 10 parts by volume per part of soap solution. The rate of feed to the column should be within a range at which an interface X will form between the water-alcohol phase and the naphtha phase at some level between the outlets for raffinate and the extract, and the phase will effectively separate from each other in the clearing zones A and B at the ends of the column.

If desired, the naphtha solution of

unsaponifiable matter may be water-washed to remove traces of soaps. The naphtha may then be evaporated from the raffinate phase to recover the unsaponifiable matter.

The concentrates of free fatty acids and unsaponifiable matter in the small residue of glyceride oil is excellently adapted for treatment in accordance with provisions of the present invention for purposes of recovering the sterols, tocopherols and other unsaponifiable constituents. In order to accomplish this result the free fatty acids and the glycerides are first converted into soaps soluble in water and alcohol.

The following examples illustrate the application of the principles of the invention in the recovery of unsaponifiable matter of soybean oil from a concentrate such as is herein described.

Example I

One thousand kilograms of a special soybean oil (by-product) derived by solvent fractionation in accordance with the provisions of the technique already described containing 4.6% unsaponifiable material (a large percentage of which was sterol in nature) and the remainder being glyceride oil, fatty acids, and other constituents was saponified in 1000 liters of methyl alcohol, and 375 liters of water with 200 kilograms of sodium hydroxide and was then diluted with 1000 liters of water. Four parts of this solution was diluted with a mixture of 2 parts of water and 1 part of methyl alcohol. The total water was 3061 liters or 3061 kilos. The total methyl alcohol was 1639 kilos or 2060 liters. It is contemplated that substantial variation in these values may at times be desired. Proportions of as low as 50% or as high as four or five-fold are contemplated. This variation may be tabulated as follows:—

	Parts by weight
By-products as soaps -	100 (upon a water free basis)
Water - - - -	153.5 to 1535
Methyl alcohol - - -	81.9 to 819

The resultant solution of saponified fatty acids and unsaponifiable matter in water and alcohol was then counter-currently extracted in an appropriate column with naphtha of about a heptane fraction. The solution is particularly well adapted to countercurrent extraction because it does not form emulsions, a difficulty characterizing many solutions. The naphtha was introduced at the bottom of the column and the soap solution at the top. The conditions of operation are tabulated as follows:—

Column temperature -	148° F.
Soap solution feed - -	65 parts (by volume per minute)
Naphtha feed - - -	120 parts (by volume per minute)

From the original 100 kilograms of extract were recovered 4.2 kilograms of unsaponifiable matter relatively rich in stigmasterol. Recovery of the unsaponifiable matter may be attained by evaporation of solvent or other appropriate method.

Example II

Two hundred pounds of extracted soybean oil by-product of the same character as that described in Example I but containing more unsaponifiable matter, was saponified with 50 pounds of sodium hydroxide in 25 pounds of water and 185 pounds of isopropyl alcohol under reflux. This solution was diluted with 530 pounds of water and extracted in the countercurrent column with a heptane fraction of naphtha. The total amount of water was 555 pounds and the total amount of isopropyl alcohol was 185 pounds. Assuming a variation of 50 to 500 per cent of these values, the range of proportions for the several components of the system may be tabulated as follows:—

	parts by weight
By-product oil as soaps	100
Water - - - -	138.8 to 1388
Isopropyl alcohol -	46.2 to 462

The solution, like that disclosed in Example I, is particularly well adapted to countercurrent extraction because it does not emulsify in such operation. The conditions of operation were as follows:—

Column temperature	106 to 125° F.
Soap solution feed -	135 (parts by volume)
Naphtha feed - -	405 (parts by volume)

The resultant naphtha concentrate of unsaponifiable matter was then further washed in a second column with water in order to remove any residual soaps remaining in solution in the naphtha. The second column was operated at a temperature of 96 to 148° F.

In this manner 12.9 pounds or 6.45 per cent of unsaponifiable matter based upon the extract treated was recovered upon evaporation of the solvent. This unsaponifiable matter represented 93.4 per cent of the tocopherol and 98.4 per cent of the total sterol content of the concentrate which was subjected to saponification.

In making up the soap solutions for extraction of the unsaponifiable matter in Examples I and II, wide variations in the ratios of the water and alcohol components to the saponified concentrate are con-

templated. The total of one or both of these components may be 50% or even less than given in the examples. On the other hand, the ratio of either or both of these components may be increased four or five fold or even more.

The alkali employed in sapnifications may be nearly molar with respect to the total of the fatty acids present as free acids or combined as triglycerides of the acids but the ratio is susceptible of considerable variation. For example, the ratio may be as much as 100% greater than molar. Usually, undue excesses are uneconomical.

As a preliminary of the saponification and extraction of the soybean oil concentrate of unsaponifiable matter as obtained from furfural or other polar solvent extraction of soybean oil, the concentrate may be subjected to treatment in order to facilitate the elimination of coloring matter in the unsaponifiable matter. In this operation the by-product or extract, before it is saponified, is treated with 22 pounds of commercial sulfuric acid dissolved in 22 pounds of water per each 200 pounds of oil. The mixture is thoroughly agitated for several hours at a temperature of approximately 170° F. The sulfuric acid may then be allowed to separate and is drawn off and the resultant treated oil or by-product oil is washed with water or, if preferred, the sulfuric acid may be left in the oil and neutralized with alkali, such as sodium hydroxide. When the by-product oil is thus treated with sulfuric acid and subjected to saponification and extraction in accordance with the provisions of the present invention, it is found that certain objectionable coloring matter initially present in the by-product is retained preferentially in the soap solution and is not extracted out into the naphtha concentrate of unsaponifiable matter.

It will be appreciated that in the foregoing examples and in similar applications of the principles of the invention, sodium hydroxide, potassium hydroxide, or ammonia or amines may be employed in the performance of the saponification operation. Methyl alcohol or isopropyl alcohol may be replaced by other of the lower alcohols such as ethyl, or *n*-propyl alcohol. Naphtha may be replaced by an ether such as diethyl ether or other ethers or by aromatic hydrocarbons such as toluene or xylene or by halogenated hydrocarbons such as ethylene dichloride or indeed by any other liquid organic solvents which are substantially immiscible with the alcohol and water solution of soaps and unsaponifiable matter.

In the extraction of the soap solution in order to remove the unsaponifiable matter, the ratio of solvent to soap solution is susceptible of wide variation though it is preferable that the solvent should at least equal the volume of the soap solution. However, any ratio of solvent to soap solution above this value can be employed. Of course, excessive increase of the volume of solvent becomes uneconomical because of the amount of solvent required to be evapoated and because of the size of the apparatus in proportion to the amount of material treated. Probably it will seldom be desired to employ a higher ratio solvent for unsaponifiable matter than 10 parts by volume to 1 part by volume of soap solution.

Example III

In accordance with the provisions of this example, a concentrate rich in tocopherol, sterols and other unsaponifiable matter of soybean oil was obtained from a by-product fraction of soybean oil resulting from extraction of soybean oil with a polar solvent as disclosed in Patents No. 658,967, 687,473 or 625,674, and subsequent extraction of the major portion of the fatty acid glycerides from the polar solvent phase with naphtha. The by-product portion rich in fatty acids, tocopherol, sterols and other saponifiable matter is retained in the polar solvent phase, and was recovered by distillation of the polar solvent.

In accordance with this example, 100 pounds of such soybean by-product of an acid value of 32, and iodine value of 137.9, a 2.51% tocopherol and 7.89% unsaponifiable matter, was treated with caustic soda in such manner as to minimize destruction of tocopherol. A satisfactory procedure involved addition of 20 pounds of sodium hydroxide, 69 pounds of water, and 125 pounds of 100% isopropanol to the foregoing quantity of by-product. Preferably the mixture of sodium hydroxide, water and isopropyl alcohol were refluxed together prior to the addition of the by-product, in order to eliminate dissolved oxygen which might adversely effect the tocopherol content of the by-product. Manifestly, if tocopherol is not to be recovered along with the other unsaponifiable matter, the refluxing procedure may be eliminated. The mixture was cooled to about 50° C. while nitrogen gas was bubbled through it, at which point the by-product was added and the mixture was refluxed while being protected with nitrogen, until saponification was complete or substantially complete. To this saponified mixture, 186 pounds of oxygen free water was added to provide a feed solution for the

Column I. Care was observed at all stages to avoid admission of oxygen to the solution. This can be attained by maintenance of a blanket of nitrogen gas over all free surfaces of the solution at all stages.

The feed solution as obtained, was of the following composition:—

	By weight
By-product (as soaps) - -	20%
Isopropyl alcohol - - -	25%
Sodium hydroxide (free and combined) - - - -	4%
Water - - - - - -	51%

Such mixture contained 0.50% tocopherol and 1.58% of unsaponifiable matter. The specific gravity of the mixture was 0.974.

The solution of soaps and unsaponifiable matter was fed in at 3 into the upper portion of the extraction zone in Column I, which in this instance was a stainless steel tube of 2 inches diameter with an inlet for solvent of unsaponifiable matter spaced 59 feet below the inlet for the soap solution. There was a 20 foot clearing section at the top of the column and a 5 foot clearing section at the bottom. The column was operated at a temperature range of 130° F. to 140° F.

In a first run, Column I was fed at 3 with 50 cc. per minute of soap solution and at 4 with a naphtha without any alcohol, at a rate of 150 cc. per minute. With naphtha alone as solvent medium for the unsaponifiable matter, difficulty of operation was experienced at these rates, owing to some emulsification of the phases with each other in their passage through the column.

In a second run, the substitution for the naphtha alone, of a naphtha feed, containing 4.76% by volume of isopropanol upon the basis of the mixture of solvents, eliminated the difficulty from emulsification and ready separation of phases was attained.

Runs were made to ascertain the maximum rate of feed in the above described column and under the conditions of operation previously described. The feed of soap solution in the last preceding example was increased in stages first to 60, then 70, then 80, then 90, and finally to 100 cc. per minute, the feeds of naphtha and isopropanol being increased proportionally. No difficulty with column flooding was experienced at any of these rates. These constitute excellent rates of feed.

The naphtha solutions of unsaponifiable matter from Column I were washed with water in Column II which was of iron and of similar diameter to Column I. The temperature of washing ranged from 105° F. to 110° F. The spacing of the inlets for wash water and naphtha solution of unsaponifiable matter in Column II was 47½ feet. Clearing sections respectively of 1¾ feet and 2 feet were maintained at the top and bottom of the Column II. The wash water feed was in a ratio of 1 to 1 with respect to the original water-alcohol-soap feed to Column I.

The recovery of available tocopherol based on the content of the original by-product was 80%. The recovery of unsaponifiable matter was 99% upon the same basis. (Percentages as herein given are by weight.)

Recovery of a fraction of increased tocopherol content from the recovered unsaponifiable matter may be effected in various ways. For example, the unsaponifiable fraction from Column II may be subjected to distillation to eliminate the naphtha. The mixture of tocopherol and other unsaponifiable matter may then be subjected to vacuum distillation preferably accompanied by hydrogenation in order to obtain a fraction of high tocopherol content. The sterols may be removed from the distillates by crystallization from solvents.

On the other hand, the unsaponifiable material may be subjected to fractional crystallization from a medium such as a mixture of 68% by volume methanol and 32% by volume of isopropyl ether. The ratio of solvent to unsaponifiable material upon a weight basis may be 4 to 1. The rate of solution of the unsaponifiable matter may be promoted by refluxing the mixture. A sterol rich fraction may be crystallized off at a temperature of 10 to 15° C. The crystals so obtained are washed with solvent to remove the intense color (yellow-red) and the sterols remaining are of straw color. They may be subjected to any further processing which may be desired.

The solution of inhibitols comprising tocopherol remaining is of intense red color. It can be processed further by distillation or hydrogenation if so desired.

Example IV

In this example, the starting material was again a by-product recovered from the furfural after extraction of the major portion of the glycerides from the furfural with naphtha in solvent fractionating soybean oil. This by-product contained 7.02% by weight unsaponifiable matter, including 1.96% by weight upon the basis of the by-product of tocopherol. The acid value was 48.9 and the iodine value was 148.4.

This material was made up into a soap solution in water and isopropyl alcohol as

in Example III and then was countercurrently extracted with naphtha of an average molecular carbon content of about 7 atoms per molecule. Column I in this example was of stainless steel packed with ½ inch Berl saddles. It was of the following dimensions:—

Diameter	6 inches
Height	88.75 feet
Upper clearing zone	3.75 feet (unpacked) plus 31.75 feet packed
Lower clearing zone	6 feet (unpacked)

The temperature ranges corresponded to those disclosed in Example III.

The feed rate was:—

Soap solution 150 milliliters per minute. The naphtha feed was varied from 150 to 600 milliliters per minute, the average being about 300 milliliters per minute. The isopropyl content of the naphtha employed for extraction varied from 2.44% to 4.76% by volume.

The naphtha extract solution was washed in Column II which was packed in the extraction zone with ½ inch Berl saddles and which was of the following dimensions:—

Diameter	3 inches
Height	87 feet, 6 inches
Upper clearing zone	22 feet, 10 inches (packed)
Lower clearing zone	6 feet, 6 inches (unpacked)

A total of 1780 pounds of by-product were so processed. A yield of 122 pounds of unsaponifiable matter, representing a percentage yield of 97% of the available unsaponifiable matter, was recovered. This contained 38.7 pounds or 31.7% of tocopherol.

About 25 pounds of the unsaponifiable matter was crystallized at 20° C. from a mixture of 70% by weight methanol, 30% by weight isopropyl ether. The crystals were washed with additional solvent. A yield of 29.5% based upon the unsaponifiables of sterols having a melting point of 137.3—138.2° C. was obtained.

The inhibitol fraction was retained in the solvent. The inhibitol constituted 4.83% on the basis of the original by-product. The tocopherol content was 1.93% on a like basis.

The following additional examples illustrate the application of the techniques of the present invention to the recovery of unsaponifiable matter, and notably of sterols, from the soap stocks from soya oil. It is preferred to split off the fatty acids combined with glycerides as free fatty acids and then distill off a considerable proportion of such acids as an intermediate step. In some cases, the stocks may contain considerable amounts of gum which may interfere with the splitting operations. This gum may be removed, in accordance with the provisions of the present invention by preliminary treating the stock with 15% sulphuric acid and washing out water soluble materials with water.

In any event, the final fatty acid mixture containing the unsaponifiable matter, before distillation, will contain from approximately 3 to 10% of unsaponifiable matter, and 80 to 97% of free acids. Residual esters may also be present. The percentage of the latter may vary from 0 to 10%. The percentages, as above given, are to be considered as being by weight. The mixtures may be distilled under vacuum, and the temperature should not be permitted to go substantially above 250° C. In this manner, a distillate constituting 75 to 95% of the charge can be obtained. Small amounts of unsaponifiable matter may also be present in the distillate. The amount will usually be within the range of 0.5 to 2% by weight. Normally, but little of the sterols will be carried over into the distillate.

The pot residue is a dark viscous liquid or even a semi-solid or waxy material. The pot residue will contain, in most instances, about 5 to 50% unsaponifiable matter including nearly all of the sterols and from 5 to 60% volatile fatty acids and polymerized fatty acids, and any glycerol esters resulting from incomplete splitting, and any wax-type esters from the sterols and other alcohols in the unsaponifiable matter. Soya acid distillation pitches generally will contain at least 20% unsaponifiable matter, of which about 50% comprises the sterols, which are rich in stigmasterol.

The sterols from the distillation residues cannot be recovered by direct methods, such as crystallization, probably because most of the sterols are tied up in the mixture in the form of esters. The saponification operations herein disclosed result in splitting of these esters and the subsequent steps of solvent extraction of the unsaponifiable matter eliminate the fatty acids as soaps from the system so that the sterols can then be separated off in relatively pure state by crystallization, or by distillation under high vacuum, or by other methods.

It is to be understood that approximately a sevenfold increase in the concentration of the sterols is secured by distillation. The pot residue or still residue will contain from 4 to 8 times as much sterol as the whole fatty acid feed stock which is subjected originally to distillation.

It must be recognized that distillation

conditions may influence yield and properties of the sterols in the distillation residue. Temperatures that are too high, or too long an exposure to more moderate temperatures may cause destruction or deterioration of the sterols. Distillation should be conducted under vacuum and at a relatively low temperature, and at as high vacuum as is practicable to attain, is preferred.

An appropriate solution system obtained from a distillation pitch from a soya soap stock acids comprises a mixture of distillation pitch in the form of soaps and unsaponifiable matter, 20% by weight; isopropanol, 25% by weight, sodium hydroxide, partially in the form of soaps, 4% by weight; and the rest (51% by weight) water.

In the saponification of the glycerides and the free fatty acids of a soap stock, a by-product from solvent fractionation, or similar source material containing relatively large amounts of unsaponifiable matter, alkali such as sodium hydroxide or potassium hydroxide preferably, is employed in sufficient excess to insure complete saponification. Usually the excess proportion will not be greater than 100% upon a molar basis.

The following examples illustrate the application of the invention to the separation of the unsaponifiable matter from a soap stock obtained in the refining of soya oil with alkali.

EXAMPLE V.

A soap stock obtained in the alkali treatment of soya oil was further treated by boiling with excess alkali to saponify the glycerides and other esters present in the original stock. This material is allowed to settle and a two phase system formed, the upper soap solution being then separated from the lower layer containing the solution of excess alkali, water and glycerol. The upper soap solution was analyzed by method G 3—39 of the American Oil Chemists Society and was found to contain 52.8% fatty acid. The remainder consisted of water and water soluble constituents. The fatty acids were found to contain 4.9% unsaponifiable matter. This soap stock in an amount of 2,000 grams was made up into solution with 4,000 grams of water and 2,660 grams of isopropyl alcohol. The solution was fed in a continuous stream into the top of a 1 inch laboratory column, 6 feet long, appropriately packed with ¼ inch Berl saddles. The clearing zones were approximately 0.5 feet top and 0.5 feet bottom. The feed rate was 7.5 cc. of soap solution per minute. A naphtha, which in this instance was paraffinic and of an average carbon content of approximately 7 carbon atoms per molecule, was fed in at the bottom of the column at a rate of 15 cc. per minute. The temperature of the column was 130° F. In a single pass through the column, 45.6 grams of unsaponified matter was separated and recovered by evaporation of the naphtha. This constituted a yield of 87.9% of the unsaponifiable matter present in the original sample. In order to separate sterols rich in stigmasterol from this unsaponifiable matter, the latter material was dissolved in acetone in a proportion of 10 parts by weight of acetone per part by weight of the unsaponifiable matter. Upon cooling the solution, the sterols separated out and were filtered. The sterols were obtained as a crystalline product having a melting point of 130 to 132 C. with a yield of 17.0 grams.

A distillation pitch as obtained by distilling a mixture of soybean acids and soybean unsaponifiable matter from a soap stock as obtained in the refining of soya oil may be substituted for the undistilled material as described in the foregoing example. Such pitch contains approximately 20% to 30% by weight of unsaponifiable matter. Sterols having a melting point of 127° C. can readily be crystallized out in a yield of 40% upon the basis of the unsaponifiable matter.

EXAMPLE VI.

In this example, a distillation pitch from a commercial soap stock obtained in the refining of soybean oil was employed as a starting material. This pitch contained 20.5 per cent. by weight of unsaponifiable matter. The remainder of the pitch was primarily fatty acids of soybean oil. For purposes of saponification, a batch was made up as follows:—

100 parts by weight of pitch
15.0 parts by weight of alkali
55.5 parts by weight of isopropanol
52.5 parts by weight of water

This batch was refluxed for 8 hours in order to attain relatively complete saponification. The resultant mixture was then diluted so that the solution to be extracted with solvent of unsaponifiable matter had the following composition:—

	By weight
Pitch (as soaps) - - -	19.1%
Sodium hydroxide - -	2.9%
Isopropanol - - - -	25.6%
Water - - - - -	52.4%

The resultant solution was subjected to counter-current extraction with naphtha of approximately heptane grade.

Run 1. In this run, an iron column of 2 inches diameter packed with ½ inch Berl saddles was employed as Column I. The column was 51 feet tall, there being

a 1.75 foot clearing zone 3a at the top and a 2 foot clearing zone 3b at the bottom. The wash Column II was also 51 feet tall and was constructed of iron. The upper clearing zone was 1.75 feet (unpacked) and the lower clearing zone was 7 feet, of which 5 feet were packed.

Soap solution was fed into the top of the column at a rate of 40 milliliters per minute and naphtha containing 4.76 per cent by volume of isopropanol was fed in at the bottom at the rate of 60 milliliters per minute. The temperature of the column was 145° F. at the top and 135° F. at the bottom.

The naphtha extract solution from the Column I was fed into the Column II at a rate of 70 milliliters per minute and was washed with an equal volumn of a mixture of 80 per cent water and 20 per cent isopropanol (percentages are by volume). The temperature of the column was 135° F. at the bottom and 143.5° F. at the top.

Run 2. In this run, a stainless steel column of 6 inches diameter was employed for purposes of countercurrent extraction of the soap solution with naphtha. The column was packed with ½ inch Berl saddles, was 88 feet, 9 inches tall with a space of 79 feet between the inlet for soap solution and the inlet for naphtha solution. A 3 foot, 9 inch unpacked clearing zone was left at the top and a 6 foot unpacked lower clearing zone was left at the bottom of the column. The soap solution was fed at 3 to the column at a rate of 300 milliliters per minute while naphtha of an average of 7 carbon atoms per molecule was in at 4 at a rate of 600 milliliters per minute. The operating temperature was 140° F. at the top and 145° F. at the bottom.

The naphtha extract solution containing a concentrate of unsaponifiable matter of the pitch, was washed in a stainless steel column of 3 inches diameter, 65 feet high packed with ½ inch Berl saddles. The inlet for naphtha solution was 6 feet. 6 inches above the bottom and the inlet for washing fluid was 55 feet from the bottom. The top clearing zone was packed. The bottom clearing one was unpacked. Wash water was fed in at a rate of 250 milliliters per minute. The naphtha extract solution was fed into the 3 inch column as it was taken off from the 6 inch column. The 3 inch column was operated at a temperature of 125° F. bottom and 130° F. bottom.

In both of these runs, at least 95% of the unsaponifiable matter in the soap solution was extracted. The unsaponifiable matter obtained by evaporation of solvent was a brownish solid.

For purposes of purification of sterols, the unsaponifiable matter was dissolved in a proportion of 1 part by weight in 10 parts by weight of a mixture comprising 30 per cent by weight of isopropyl ether and 70 per cent by weight of methanol. In order to obtain solution of the solids, the solvent was refluxed and the resultant mixture was filtered while hot to remove any suspended matter contained therein. The solution was cooled to 20° C. and the crop of crystals which came down was filtered off, washed and dried. The product had a somewhat brownish color but the melting point was within the range of 134 to 135° C. The yield was 49.7 per cent of the unsaponifiable matter, or 10.3 per cent based upon the original pitch. The color of the crystals could be improved by recrystallization and/or treatment of the solution thereof with activated carbon. In many instances, such decolorization treatment apparently would not be required.

The extracted soap solution obtained in the foregoing treatment was acidified and the free fatty acid layer was water washed and dried. The fatty acids were then distilled under vacuum to yield 58.7 per cent by weight of distilled acids of an iodine value of 95.1, acid value of 193.7. The product was a semi-solid at room temperature.

Example VII

Substitute methyl alcohol for isopropyl alcohol in any one of the preceding examples and proceed as outlined in the example.

Example VIII

Substitute ethyl alcohol for isopropyl alcohol in any of Examples I through VI and proceed as outlined in the selected example.

Example IX

Substitute propyl alcohol for isopropyl alcohol in any one of Examples I through VI and proceed as outlined in that example.

In accordance with the preferred embodiment of this invention, the proportions of alcohol in the initial solution fed to the column near the top thereof may be substantially lower than has heretofore been stated. However, the use of high percentages of alcohol in the initial solution are permissible if especially rapid countercurrent permeation of the liquid phases through each other is desired.

In accordance with this embodiment, a substantial proportion of the total alcohol employed in the system in Column I is added in the solvent, e.g., naphtha, of unsaponifiable matter, which is fed into the lower zones of the column as indicated at 4 in the drawing. The amount of lower water soluble alcohol added in this

solvent of unsaponifiable matter will vary, dependent upon the source of the saponified material which is undergoing treatment. For example, the mixture of soaps of tall oil acids and tall oil unsaponifiable matter as obtained from treatment of tall oil or from treatment of tall oil distillation residues with alali, when properly proportioned with water and lower alcohol, is relatively easy to fractionate by countercurrent treatment of the solution of said saponified material in water and a lower water soluble alcohol, even without added lower alcohol in the solvent of unsaponifiable matter. In such case, the lower water soluble alcohol is merely added further to improve the operation and to avoid possible emulsion formation. Fairly small amounts of alcohol may be added to the solvent of unsaponifiable matter such as naphtha, however, it will be apparent that no harm is done if substantial amounts of alcohol are included in the naphtha feed, though of course, the inclusion of such excesses are not economical. Naturally, where an alcohol is added to the feed of naphtha at inlet 4, a reduction can usually be made in the alcohol in the solution fed in at 3. Of course, enough lower water soluble alcohol must be present in the initial solution to attain solution of soaps and unsaponifiable matter. Beyond this requirement, the rest required to attain smooth operation can be fed in with the solvent of unsaponifiable matter.

Where mixtures of soaps and unsaponifiable matter from wool grease or from oils such as soybean oil, or from soap stocks from such oils are to be treated, it is preferable to employ substantially more of the lower, water-soluble alcohol in the naphtha feed.

Very good results have been obtained by employment of about 5% of isopropyl alcohol in naphtha based upon the volume of the solvent, as the solvent of unsaponifiable matter. It is doubted that the percentage of the lower water soluble alcohol should be much less than approximately 1 per cent by volume of the alcohol-naphtha solution. On the other hand, the percentage of such alcohol may well substantially exceed the 5% above referred to. The percentage upon a volume basis of the alcohol may well extend up to 10 or even 20% by weight of the naphtha or like solvent introduced.

In referring to the solvent of unsaponifiable matter, especial emphasis has been placed upon naphtha. It is probably one of the most satisfactory materials for the purpose from the standpoint of costs and operating efficiency. However, the invention also includes the use of other solvents of unsaponifiable matter which have a reasonable solubility with the alcohol component of the alcohol-water solution employed as a solvent of the unsaponifiable matter-soap mixture. Typical solvents of this character are hexane, heptane, octane, nonane, decane, and like aliphatic hydrocarbons, or aromatic hydrocarbons, ethers or halogenated hydrocarbons such as ethylenedichloride compatible with the lower alcohol.

The ratios of the feeds of alcohol-water solution of soaps and unsaponifiable matter, and the solution of water soluble lower alcohol in solvent of unsaponifiable matter, is susceptible to considerable variation. The proportions of these feeds, as well as temperatures, may safely vary, for tall oil with a small amount of lower alcohol being included in the naphtha feed. As previously stated, the mixture of soaps from tall oil acids and tall oil unsaponifiable matter in water and a lower water soluble alcohol, is usually comparatively easy to fractionate in a countercurrent system, when the several components of the system are proportioned. However, where it is desired to increase the rate of flow of the constituents in the system, or otherwise to promote efficiency of operation, a small amount, e.g., 1 to 10% or 20% of an alcohol such an ethanol, methanol, or isopropyl alcohol can be included in the naphtha feed to the Column I. The percentages herein specified are to be considered as being by volume and being based upon the mixture of naphtha and lower water soluble alcohol. The alcohol component in the water-alcohol mixture acting as the solvent of unsaponifiable matter-soap mixture, can be reduced by an amount at least equivalent to the alcohol which is introduced with the solvent of unsaponifiable matter. Sometimes the percentage of lower alcohol in the soap feed can be even further reduced.

The use of lower water soluble alcohol in the solvent of unsaponifiable matter, as employed in the removal of said matter from a solution of soaps of wool fat acids and wool fat unsaponifiable matter in a mixture of water and a lower water soluble alcohol is quite advantageous. In the separation of wool fat unsaponifiable matter from a mixture of such matter and soaps of wool fat acids obtained by subjecting wool fat to treatment with an alkali, such as sodium hydroxide, a solution of the soaps and the unsaponifiable matter may be made up by dissolving a mixture of said soaps and unsaponifiable matter in water and a lower water soluble alcohol to provide a solution containing 5 ·· 30% by weight of the soaps and the unsaponifiable matter the alcohol consti-

tuting about 5% up to about 70% by weight of the water-alcohol mixture.

For purposes of extracting the unsaponifiable matter from this solution, the solution may be fed in at 3 and contacted countercurrently in the Column I with a solvent of said unsaponifiable matter which is immiscible with, or at least but partially miscible with the water-alcohol solution. The solvent of unsaponifiable matter may be employed in a proportion of about 1 to 20 parts by volume per part of the solution of soaps and unsaponifiable matter in the mixture of water and lower water soluble alcohol. Of course, the extraction of unsaponifiable matter is effected by mutually countercurrently flowing the two liquid phases through each other in the manner already described.

The temperature in the extraction Column I preferably, should be in a range of about 80 to 180° F. Assuming that naphtha is employed as the solvent of unsaponifiable matter, a paraffinic naphtha, which is liquid and of a boiling range of about 80 to 130° C. is to be preferred.

The solution of unsaponifiable matter in the mixture of solvent and lower water soluble alcohol passing out at the top of the Column I may be passed to Column II as previously described where it is subjected to washing with water or a mixture of water and a lower water soluble monohydric saturated alcohol such an ethanol, isopropyl alcohol, methanol or the like. The proportion of water or water and lower alcohol so employed, need only be sufficient to reduce the soap content of the solution of unsaponifiable matter to a reasonable value. Proportions by volume of water within a range of 0.2 to 3.0 parts per part of solution to be washed are contemplated.

The Column II may conveniently be operated at a temperature within a range of approximately 80 to 180° F. in the manner already described in connection with Column I. The optimum temperature ranges for both columns would appear to be approximately 125 to 150° F.

The conditions for operation of the Column I and II may be summarized as follows:—

COLUMN I

Solutions

Water-alcohol mixtures	Water—60—90% Alcohol—10—40%
Soap feed composition	Water—alcohol—95—60% Solids—5—30%
Solvent of unsaponifiables	Solvent—80—99% Lower alcohol—1—20%

(Percentages are by weight of solutions.)

Feed Ratios

Soap solution	1 part by volume
Solvent of unsaponifiables	1—20 parts by volume
Temperature of Column I	80—180° F.

COLUMN II

Wash water	0.2—60.0 parts by volume per part by volume of original soap feed
Naphtha unsaponifiable	1—20 parts by volume per part by volume of original soap feed
Temperature of Column	80—180° F.

The following examples illustrate the application of the principals of the preferred embodiment to the separation of unsaponifiable constituents from fatty materials from various sources.

EXAMPLE X

In this example, a distillation pitch from a soap stock obtained in the refining of soybean oil was employed as a starting material. This pitch contained 20.5% by weight of unsaponifiable matter. The remainder of the pitch was primarily fatty acids of soybean oil. For purposes of saponification a batch was made up as follows:—

100	parts by weight (water free basis) of pitch
15.0	parts by weight of alkali (NaOH)
55.5	parts by weight of isopropanol
52.5	parts by weight of water

This batch was refluxed for 8 hours in order to attain saponification of the free fatty acids. The resultant mixture was then diluted so that the solution to be extracted had the following composition:—

	by weight
Pitch (water free basis in a saponified form) - -	19.1%
Sodium hydroxide (free and combined - - - -	2.9%
Isopropanol - - - -	25.6%
Water - - - -	52.4%

The resultant solution was then subjected to continuous countercurrent extraction with petroleum naphtha averaging about 7 carbon atoms per molecule in an iron Column I of 2 inches diameter and being packed with ½ inch Berl saddles. The column was 51 feet tall and the space between inlet 3 for soap solution and inlet 3 for naphtha, was approximately 47.25 feet, there being a 1 foot, 9 inch unpacked clearing zone CU at the top and a 2 foot, 9 inch unpacked clearing zone CL at the bottom.

Soap solution was fed into the column at inlet 3 at a rate of 40 milliliters per minute and naphtha containing 4.76% by volume of isopropanol was fed in at inlet 4 at a rate of 60 milliliters per minute. The temperature of the column at the top was 145° F. and 135° F. at the bottom.

Column II, which was employed to wash the naphtha extract solution from Column I was of iron, was packed with ½ inch Berl saddles and was 51 feet tall. It had an unpacked upper clearing zone of 1.75 feet and a bottom clearing zone of 7 feet, 5 feet of which was packed with ½ inch Berl saddles, there being a 2 foot gap between the packing in the upper part of the column and that in the lower part. The top of the column was held at 143.5° F., while the bottom was at 135° F.

The naphtha extract solution from the Column I was fed into the Column II at a rate of 70 milliliters per minute and was washed with an equal volume of a mixture of 90% by weight of water and 10% by weight of isopropanol.

In the run, at least 95% of the unsaponifiable matter in the soap solution was extracted. The unsaponifiable matter was obtained as a brownish solid, which was recovered by evaporation of the solvent medium.

For purposes of purification of sterols, the unsaponifiable matter was dissolved by refluxing in a mixture comprising 30% by weight of isopropyl ether and 70% by weight of methanol. The resultant solution was filtered while hot to remove any suspended matter contained therein. Subsequently, it was cooled to 20° C. and the crop of crystals which came down was filtered off, washed and dried. The product had a somewhat brownish color but the melting point was within a range of 134 to 135° C. The yield was 49.7% of the unsaponifiable matter or 10.3% based upon the original pitch. The colour of the crystal could be improved by recrystallization and/or treatment of the solution thereof with activated carbon. In many instances, decolorization treatment apparently would not be required.

The soap solution remaining after extraction of the unsaponifiable matter, was acidified and the free fatty acid layer was water washed and dried. The fatty acids were then distilled under vacuum to yield 58.7% by weight of distilled acids of an iodine value of 95.1, and an acid value of 193.7. The product was a semisolid at room temperature.

Example XI

In this example, a soybean oil by-product obtained from the solvent fractionation of the soybean oil with furfural was employed as a starting source material. This material contained considerable amounts of tocopherol, a material of considerable value, and attention was given to the recovery of this material in undegraded form along with the other unsaponifiable matter. In addition to tocopherol, the material contained free fatty acids of soybean oil, glycerides of soybean oil and unsaponifiable matter such as sterols including stigmasterol. The properties of the by-product material were as follows:—

Iodine value - - - -	137.9
Acid value - - - -	32.5
Per cent tocopherol - -	2.51
Per cent unsaponifiable matter - - - - -	7.89

For purposes of effecting the saponification of the by-product, a batch of the following composition was made up which, upon the basis of each 100 pounds of water free by-product was of the composition:—

By-product - - -	100 pounds
Sodium hydroxide -	20 pounds
Water - - - -	69 pounds
100% isopropyl alcohol	125 pounds

In preparing the batch, water and alcohol can be made up as a separate solution, if so desired.

In order to obviate the destruction of tocopherol, saponification of this material

was conducted under nearly oxygen free conditions. To this end, as preliminary step to the saponification, all of the foregoing constituents except the by-product, were brought together and refluxed in order to remove any dissolved oxygen. The deoxygenated solution was then cooled to 50° C. while nitrogen gas was bubbled therethrough in order to sweep out any oxygen which might get into the system. The by-product was then added and the mixture was brought to reflux temperature and maintained at such temperature for 2 hours while nitrogen was continually bubbled through the mixture, in order to assure as nearly oxygen free conditions as could be attained. Subsequently for each 100 pounds of by-product 186 pounds of water, free of dissolved oxygen, was added and the soap feed solution was protected by nitrogen gas at all times.

The composition of the feed solution as fed to the Column I was as follows:—

	By weight
By-product	20%
Isopropyl alcohol	25%
Sodium hydroxide (free and combined)	4%
Water	51%

This solution contained approximately 0.5% by weight of tocopherol and 1.08% of unsaponifiable matter. The specific gravity was found to be 0.974.

For purposes of extracting the unsaponifiable matter from this solution, a stainless steel column of 2 inches diameter was employed as Column I. The space between the inlet of soap solution and naphtha was 59 feet. There was a clearing section of 20 feet at the top of the column and a second clearing section of 5 feet at the bottom.

The naphtha solution from the column was continuously countercurrently washed with water in a second column (II) of iron which was 47.25 feet between the inlets of naphtha and soap solution and had a top clearing section of 1.75 feet and a bottom clearing section of 2 feet.

The operating conditions for Column I were as follows:—

Soap feed	50 milliliters
Naphtha feed containing 4.76% by volume isopropanol	150 milliliters
Temperature top	140° F.
Temperature bottom	130° F.

The conditions of operation for Column II were as follows:—

Feed — The naphtha extract from Column I

Wash Water—50 milliliters per minute

Temperature—Top—110° F.

Temperature—Bottom—105° F.

The solvent was distilled off from the naphtha phase to recover the unsaponifiable matter.

The recovery of tocopherol, based on the content determined analytically upon the original by-product, was 80%. The recovery of unsaponifiable matter was 99% calculated upon the same basis.

The unsaponifiable matter as obtained from the naphtha solution from Column II was worked up as follows:—

The unsaponifiable matter was dissolved in an appropriate solvent medium of which a number were tested. The ratio of solvent was 5 milliliters per gram of unsaponifiable matter. Of several solvents tested, one comprising 32% isopropyl ether and 68% methanol (percentages by volume) was found to be exceptionally satisfactory. The unsaponifiable matter was dissolved by refluxing the solvent medium, refluxing being continued until solution was complete. The solution was then cooled to about 10 to 15° C. and the resultant crop of crystals comprising primarily the sterols of the unsaponifiable matter, were filtered off and washed with enough solvent to remove the intense reddish-yellow color resultant from adherent tocopherol or inhibitol. In this washing operation, 1 to 1.5 milliliters per gram of unsaponifiable matter was found to be sufficient. The sterols after removal of the solvent, were a straw color and of high melting point.

The solution of inhibitols remaining in the solvent is very rich in tocopherol and is of an intense red color. It can be processed further by distillation under vacuum or hydrogenation.

The temperature of distillation may be carried to about 300° C. and about 90% of the tocopherol in the original inhibitol fraction can be so recovered.

If desired, the tocopherol may be deodorized by steam under a temperature of 125° C. and a pressure of 4.5 millimeters absolute.

The results attending the use of several systems of solvents as above outlined for crystallizing out sterols are tabulated as follows:—

Solvent Type (% by volume)	Cooling Temp. °C.	Original U.M. % Toc.	Sterols % Yield	Sterols M.P.	Appearance	Inhibitol Fraction % Yield	Inhibitol Fraction % Toc.
Acetone	−5	28.4	36.7	138 —139.6	Straw colored	63.3	46.6
Acetone	−2	20.7	27.4	137.8—138.2	Straw colored	70.3	40.2
Acetone	−2	21.8	27.6	135.0—136.0	Straw colored	60.0	35.6
Acetone	−2	28.0	32.1	135.6—136.4	Brownish tint	—	—
60% Acetone 40% Alcohol	20	28.0	30.4	137.6—138.5	Brown	—	—
32% I.P.E. 68% Methanol	19	28.0	31.9	138.6—139.4	Cream colored	—	—
30% Naphtha 70% Methanol	8	28.0	22.9	137.0—137.6	Brown	—	—
30% Benzene 70% Methanol	8	28.0	10.8	134.8—135.4	Brown	—	—
32% I.P.E. 68% Methanol	8	28.0	34.1	135.8—136.6	Straw colored	66.4	45.0
32% I.P.E. 68% Methanol	10	—	31.3	136 —137	Straw colored	69.1	45.4
32% I.P.E. 68% Methanol	10	32.4	28.1	137.4—138	Straw colored	71.8	42.2
32% I.P.E. 68% Methanol	14	28.0	33.9	135.6—136.6	Straw colored	66.1	43.5
32% I.P.E. 68% Methanol	14	28.0	34.5	136.4—137.0	Straw colored	65.5	42.7
32% I.P.E. 68% Methanol	14	—	24.8	135.8—136.4	Straw colored	75.2	44.3

In the table, the initials "I.P.E." designate isopropyl ether. "Toc." designates tocopherol. The percentages given in the solvent column are by volume. The percentages in the column under the heading "Original U.M." are the percentages by weight of tocopherol as contained in the original unsaponifiable matter. The percentages in the column under the heading "% Yield" comprise the percentages of sterols contained in the unsaponifiable matter. Under the column headed "Appearance" the color of the sterol fraction is designated. The two columns under the heading "Inhibitol Fraction" are respectively the yield of inhibitol based upon the original inhibitor in the original unsaponifiable matter and the percentages as given in the second column under the heading "Inhibitol Fraction," designate the percentages by weight of tocopherol contained in the inhibitol fraction.

Example XII.

In this example a by-product from the furfural extraction of soybean oil, corresponding to that described in Example XI, was employed. The by-product was saponified and made up into solution in water and isopropyl alcohol in the manner described in the latter example. The by-product contained 1.96% tocopherol and 7.02% unsaponifiable matter (percentages by weight). The average iodine value was 148.4 and the acid value was 48.9.

A total of 1,780 pounds of this by-pro-

duct was saponified, made up into solution for extraction with naphtha in the manner hereinafter to be described. The by-product was saponified, made up into solution and extracted in a 6 inch stainless steel column, 88 feet, 9 inches higher, packed with ½ inch Berl saddles. It had an upper clearing zone of 31.75 feet packed and 3.75 feet unpacked and a lower clearing zone of 6 feet unpacked. The soap feed rate was 150 to 225 milliliters per minute and the naphtha feed rate was from 150 to 600 milliliters per minute. However, most of the run was at a soap feed of 150 milliliters and a naphtha feed of 300 to 400 milliliters per minute. The naphtha feed employed in these runs included 4.76% by volume of isopropanol. About 95% of the tocopherol present in the original by-product was extracted.

The naphtha solution was washed free of soaps with water in a 3 inch iron column, 87.5 feet high, packed with ½ inch Berl saddles, with an upper clearing zone of 22.8 feet (partially packed) and a lower clearing zone of 6.5 feet (unpacked). The naphtha solution could, if desired, be partially (e.g., 50 to 90%) stripped of naphtha before it is washed.

From a total of 1,780 pounds of by-product, there was recovered 122 pounds of unsaponifiable matter representing a yield of 6.85% or 97.5% of the amount indicated by analysis. The unsaponifiable matter composite, contained 31.7% by weight of tocopherol which represented a yield of 2.17% by weight based on the original by-product.

Twenty-five pounds of the unsaponifiable matter obtained as above described, was crystallized from a mixture of 70% by weight of methanol and 30% by weight of isopropyl ether at a temperature of 20° C. The crystals were washed with additional solvent and a yield of 29.5% sterols with a melting point of 137.3 to 138.2° C. was obtained. The sterols constituted 2.02% by weight of the by-product. The inhibitol fraction remaining in the solvent constituted 40.1% by weight of the unsaponifiable matter representing 4.83% by weight of the original by-product. The yield of tocopherol obtained by distillation of the inhibitol fraction was 1.93% by weight based on the by-product employed as a source material.

Example XIII

This example applies to the extraction of the unsaponifiable matter of wool grease from a mixture of crude wool grease including fatty acids, sterols such as cholesterol, tri-terpine alcohols and other constituents. A soap composition was made up from this crude wool grease having the following composition:—

Crude wool grease	200 pounds
Isopropanol	111 pounds
Water	105 pounds
Sodium hydroxide	30 pounds

The mixture was refluxed for 17 hours.

Since the resultant soap mixture did not appear to be fully saponified, an additional 10 pounds of sodium hydroxide was added and the material was refluxed overnight. The resultant soap mixture was made up into solution of the following composition:—

	by weight
Wool grease	14.3%
Isopropanol	22.6%
Water	60.2%
Sodium hydroxide	2.9%

This solution was subjected to extraction in naphtha in a stainless steel column of 2 inches diameter having a space of 59 feet between the inlets for solvent and soap solution with appropriate clearing zones, about 23.5 feet, at the upper end and about 5 feet at the lower end. A 2 inch column of iron was employed for the water washing of the naphtha solution of unsaponifiable matter obtained. It corresponded to the Column II described in Example II.

The soap solution was subjected to intimate countercurrent contact in the Column I with a petroleum naphtha (of an average of 7 carbon atoms per molecule) containing 4.76% of isopropanol by volume. The soap feed to the column was 30 milliliters per minute. The naphtha feed was 60 milliliters per minute. The column was maintained at 145° F.

The naphtha extract solution from the first column was subjected to washing with an aqueous mixture comprising 80% water and 20% isopropanol by volume in Column II, the feeds being the naphtha extract solution from the first column, the aqueous isopropyl alcohol solution being in a proportion of 60 milliliters per minute. The column was operated at a temperature of 135° F. The recovery was 97% of the total unsaponifiable matter from the naphtha extract solution. The recovery of total unsaponifiable matter was almost theoretical.

Example XIV

A second run was then conducted with wool grease as above described, the apparatus being the same as in Example XIII. The wool grease was saponified by treatment in a batch of the following composition:—

Crude wool grease	100 pounds
Isopropanol	55.5 pounds
Water	52.5 pounds
Sodium hydroxide	15 pounds

The saponification reaction was conducted over a period of 6 hours. A sample of unsaponifiabe matter isolated from the batch at the conclusion of this time, had a good color and a saponification value of 1.8. The batch was then diluted with 71.5 pounds of isopropanol and 374 pounds of water. 71.5 pounds of naphtha was also included though it has been found that this component is unnecessary.

The composition of the batch upon a naphtha free basis was:—

14.3% by weight of wool grease
22.5% by weight of isopropanol
61.1% by weight of water
2.15% by weight of hydroxide

The solution was then extracted by countercurrent contact with naphtha in the Column I described in Example X, the feeds being soap solution 35 milliliters per minute, naphtha containing 5% of isopropyl alcohol, 60 milliliters per minute. The temperature of operation was 145° F. Under these conditions, the column operated quite satisfactorily.

The solution from the Column I comprising the naphtha and unsaponifiable matter was then water washed in a second Column II which was the same as described in Example X. The feed of unsaponifiable matter was 70 milliliters per minute which was countercurrently washed in the column with a mixture comprising 20% by volume of isopropanol and 80% by volume of water, the feed of the washing solution being 70 milliliters per minute. The temperature of column was 135° F. The solution of unsaponifiable matter in naphtha was then subjected to distillation in order to eliminate the naphtha contained therein. The resultant unsaponifiable matter as recovered, was acceptable in regard to color and other characteristics.

Example XV

Substitute soybean oil for soybean by-products in Example XI and proceed as in the latter example. The yields of unsaponifiable matter obtained in this example, of course, will be much lower than in Example XI owing to the fact that the concentration of such unsaponifiable matter in the starting material is relatively low.

Example XVI

Substitute sugar cane wax or sugar cane oil for soybean by-product in Example XI and proceed as in the latter example.

Example XVII

Substitute cotton seed oil for soybean oil by-product in Example XI and proceed as in the latter example.

Example XVIII

Substitute fish oil, e.g., cod liver for soybean by-product oil of Example X and proceed as in that example.

While the process has been described with reference to embodiments in which the naphtha or like solvent and the lower alcohol are introduced together through the same inlet, it is to be understood that the alcohol and the naphtha may be separately introduced. Preferably the lower alcohol is introduced into the column near the point where the naphtha is introduced. However, the alcohol may be introduced at a point intermediate the naphtha and the soap solution inlet or even below the naphtha inlet.

The countercurrent extraction of the unsaponifiable matter from the soap solutions in vertically elongated towers or columns constituting extraction zones, has been particularly emphasized. However, it will be understood that other types of apparatus may also be employed in the performance of the countercurrent extraction. For example, it is contemplated to employ centrifuges including involutely coiled perforated diaphragms disposed to rotate about their axis. Naphtha is fed in at the outer periphery and solutions of fatty acids, unsaponifiable matter and the like in water and alcohol can be fed in axially. Apparatus of this type is disclosed in such United States patents as 2,209,577; 2,281,796; 2,109,375, 1,936,523; and 2,286,157. In the apparatus of the type disclosed in these patents, the liquid phase of lower density fed in at the outer periphery permeates inwardly toward the axis and the heavier soap solutions fed in at the axis permeate outwardly. The two phases are drawn off at the respective limits of their paths of travel in the centrifuge by means of appropriate devices not constituting a part of this invention and therefore not specifically illustrated.

What we claim is:—

1. A process of obtaining unsaponifiable matter of a glyceride oil containing said matter, which process comprises treating with alkali, a solution comprising 3 to 50 per cent. of said unsaponifiable matter, dissolved in a mixture of glycerides of said oil, and free fatty acids of said oil, or soaps of said acids, whereby to convert the glycerides and any free fatty acids present into soaps, making up the mixture of soaps and unsaponifiable matter in a proportion of 100 parts by weight upon a water free basis into a soap dispersion in water in a proportion of 146 to 1460 parts by weight and a lower monohydric, saturated, alkyl alcohol containing 1 to 3 carbon atoms, in a proportion of 61 to 610

parts by weight, flowing the resultant soap dispersions counter-currently with solvent of unsaponifiable matter insoluble in the solution in an extraction zone in a proportion of 1 to 10 parts by volume per part by volume in an extraction zone in a proportion of 1 to 10 parts by volume per part by volume of the soap dispersion, recovering a solution of unsaponifiable matter in said solvent from said extraction zone and evaporating the solvent to recover the unsaponifiable matter contained therein.

2. A process according to Claim 1, in which the solvent of unsaponifiable matter is naphtha.

3. A process according to Claim 1 or 2, in which the alcohol is isopropyl alcohol.

4. A process according to Claim 1 or 2, in which the alcohol is methyl alcohol.

5. A process according to Claims 1 to 3, in which the glyceride oil is soybean oil and the mixture contains from 4 to 30% of unsaponifiable matter of soybean oil and 5 to 40% of free fatty acids of soybean oil, and in which after the treatment with alkali the mixture of soaps and unsaponifiable matter is made up into a soap dispersion in which the water is present in a proportion of 277.5 to 2775 parts, and the alcohol is present in a proportion of 92.5 to 925 parts for each 200 parts of the mixture.

6. A process according to Claima 1 to 3, in which the solution to be treated is that resulting from the solvent extraction of soybean oil with furfural to obtain a solution of highly unsaturated glycerides, sterols, inhibitols, and free fatty acids, in furfural, extracting out most of the glycerides from the solution with naphtha, and evaporating the furfural in the residual solution, and in which the soaps and unsaponifiable matter is made up into a soap dispersion in which alcohol is employed in a proportion of 185 pounds for each 200 pounds of the concentrate prior to saponification, the solution being diluted with 555 pounds of water.

7. A process according to Claims 1 to 3, in which the solution to be treated with alkali is the by-product obtained by extracting soybean oil with furfural, washing the furfural solution, rich in unsaturated glycerides and unsaponifiable matter, with naphtha to remove glycerides, then recovering said by-products from the furfural, and in which the soaps of fatty acids of soybean oil and unsaponifiable matter of soybean oil are made up into a soap dispersion comprising for each 100 parts by weight upon a water free basis of the by-product subjected to saponification, 46.2 to 462 parts by weight of isopropyl alcohol and 138.8 to 1388 parts by weight of water.

8. A process according to Claims 1, 2 and 4, in which the solution to be treated with alkali is the by-product obtained by extracting soybean oil with furfural, washing the furfural solution, rich in unsaturated glycerides and unsaponifiable matter with naphtha to remove glycerides, then recovering said by-product from the furfural and in which the soaps of fatty acids of soybean oil and unsaponifiable matter of soybean oil are made up into a soap dispersion comprising for each 100 parts of by-product, 81.9 to 819 parts of methyl alcohol and 153.0 to 1530.0 parts of water.

9. A process according to any one of the preceding claims, in which the solution of unsaponifiable matter in the solvent is washed with water prior to the evaporation of the solvent.

10. A process according to any one of the preceding claims, in which prior to making up the mixture of soaps and unsaponifiable matter the soaps are acidified to liberate free fatty acids, free fatty acids are selectively distilled off from the unsaponifiable matter, and the still residues are subjected to saponification with alkali in order to convert the free fatty acids therein into soaps.

11. A process according to any of the preceding claims, in which sterols in the unsaponifiable matter are separated from the remainder of the unsaponifiable matter e.g. by crystallization.

12. A process according to any one of the preceding claims, in which the extraction zone is elongated and the soap dispersion is introduced into the upper portion of the extraction zone and the solvent is introduced into the lower portion of the same zone.

13. A process according to any one of the preceding claims, in which the solvent of unsaponifiable matter is fed into the extraction zone with additional lower water soluble alcohol.

14. A process according to Claim 13, in which the solvent of unsaponifiable matter and the lower water soluble alcohol are introduced into the extraction zone in a common stream.

15. A process according to Claim 12, in which the solvent of unsaponifiable matter and an additional lower water soluble alcohol are introduced into the elongated extraction zone in separate streams.

16. A process according to Claim 15, in which the additional lower water soluble alcohol is introduced into the extraction zone at a point near the point of solvent introduction.

17. A process according to Claim 15 or

16, in which the additional lower water soluble alcohol is introduced into the extraction zone between the point of soap dispersion feed and and the point of withdrawal of the solution of unsaponifiable matter.

18. A process according to Claim 16, in which the soap dispersion is fed into the extraction zone at the inlet near to but spaced from one end thereof, and the solvent is fed into the zone at an inlet near to, but spaced from, the other end of the zone, the additional lower water soluble alcohol being introduced at a point on the same side of the first mentioned inlet as is the second mentioned inlet.

19. A process according to any one of the preceding claims, in which alcohol comprising 10 to 40 per cent. of the solution of soaps and unsaponifiable matter is flowed counter-currently with a solution of naphtha and 1 part by volume of said solution is fed into said zone, 1 to 20 parts by volume of a solution of naphtha and a lower water soluble monohydric alcohol containing 1 to 20 per cent. by volume of said alcohol.

20. A process of obtaining unsaponifiable matter of a glyceride oil containing said matter substantially as hereinbefore described and as illustrated in the accompanying drawings.

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